DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS
WASHINGTON, D. C.

Letter
Circular
28

(December 9, 1921.)
(Revised December 1, 1925).

***

Anti-Freezing Solutions for Automobile Radiators

***

The Bureau of Standards has studied the properties of many liquids proposed for winter use in automobile radiators and the information here presented is intended to aid the motorist (1) in selecting a suitable radiator liquid and (2) in using it effectively.

Oil cooling is used to a considerable extent in heavy duty tractors but a cooling system designed to use oil instead of water requires in general a more rapid rate of circulation on account of the relatively low heat capacity, and larger or less obstructed passages on account of the relatively high viscosity of most oils. Hence the average automobile cooling system designed for use with water will not handle heavy oils successfully. Kerosene can be used in automobile cooling systems provided with mechanical circulation but the odor and inflammability of its vapor, the possibility of overheating due to its high boiling point, and its solvent effect on rubber are objections to its use. The higher operating temperature which it gives may be an advantage especially in cars whose radiators normally give excessive cooling.

With the above exception, the radiator liquids actually used are almost exclusively aqueous solutions. The first requirement of an anti-freezing solution is that it shall not injure either engine or radiator by freezing at the lowest temperature which may be encountered. To be satisfactory, however, such a solution should (a) cause no damage to the cooling system through solvent action or corrosion and (b) circulate freely at the lowest operating temperature. While these are essential requirements, they are not the only ones, as will be seen from the discussion of various solutions considered below.

The corrosive effects of various solutions upon the metals commonly employed in radiator construction have been investigated by the Bureau. Inasmuch as electrolytic action on dissimilar metals in contact is largely responsible for radiator corrosion, corrosion effects upon the combinations of metals ordinarily used in radiators were studied. Such tests showed that practically all salt solutions cause appreciable corrosion while solutions of organic materials (such as sugar, alcohol, or glycerine) when free from electrolytes cause no more corrosion than ordinary tap water.

Solutions of Salts ($CaCl_2$, $MgCl_2$, etc.)

Calcium Chloride

Calcium chloride preparations are sold under a variety of names. While they will prevent freezing down to temperatures as low as -50°C (-58°F), if properly prepared, solutions of calcium chloride and water are known to have a corrosive action on the engine jacket, on the solder in the radiator, and on aluminum which is sometimes used in manifolds, pumps, and headers. The effect on solder and aluminum is especially serious. Certain calcium chloride preparations contain a small amount of a soluble chromate added for the purpose of retarding this corrosive action. Laboratory tests at this Bureau indicate that the addition of a soluble chromate may be effective in preventing corrosion except in the case of aluminum.

A very troublesome effect of all calcium chloride solutions is experienced if the solution comes in contact with spark plugs or ignition wires. The salt deposited when the water evaporates is very difficult to remove and when it cools it absorbs water and becomes a good electrical conductor causing short circuits which are not easy to locate as they disappear when the engine is heated up.

Magnesium Chloride

During the winter of 1924-25 considerable quantities of magnesium chloride solution were sold for radiator use under a trade name and were guaranteed to be "no more harmful than water". Magnesium chloride solutions are more corrosive than calcium chloride solutions and no effective means of retarding their corrosive action, by the addition of a second salt or otherwise, has been brought to the attention of this Bureau. The maximum protection which this salt can give is to prevent freezing down to -33.5°C (-28°F).

Other Salts

The behavior of calcium chloride solutions, discussed above, appears to be typical of all other salt solutions.

Solutions of Sugars (Honey, Invert Sugar, Glucose)

Honey

Bee-keepers have long advocated the use of honey solutions in automobile radiators, as an outlet for their lower grades.

Recent tests at this Bureau gave the following results:

% Honey (by volume)	Freezing Point °C	°F	Density at 21°C grams/ml
33 1/3	-6	+21	1.165
50	-10	+14	1.222
66 2/3	-17	+ 1	1.275
75	-23	- 9	1.307
100	--	--	1.403

Objections to anti-freezing solutions of honey in water are that low percentage mixtures do not have sufficiently low freezing points and high percentage mixtures are so viscous that they circulate very slowly, if at all. In case circulation stops, charring of the honey in contact with the hot engine is quite likely. These solutions, like many others, are not likely to cause bursting until cooled several degrees below the freezing points given, as slush begins to form at the freezing point and only gradually becomes solid. The use of these solutions does not remove the other ill effects of freezing, such as injury to the circulating pump and overheating of the engine due to lack of circulation.

If a honey-water solution is heated to boiling and a small amount of alcohol is added, certain starchy impurities are precipitated and may be filtered out. A solution thus treated is clear, less viscous and has a somewhat lower freezing point than the original solution on account of its alcohol content. The addition of an excess of alcohol, however, may cause sugar to crystallize out, thus increasing the likelihood of clogging the radiator passages.

Invert Sugar

The sugar in honey being invert sugar (dextrose and levulose) solutions of commercial invert sugar were also proposed for radiator use. As 66 2/3% and 75% honey solutions contain roughly 55% and 60% of invert sugar by weight, invert sugar solutions of these strengths were prepared and tested. Their freezing points (-16°C and -22°C) agreed with those of the corresponding honey solutions. The same objections hold for these as for honey solutions.

Glucose

Glucose solutions are much less effective than honey solutions. Dextrose is the essential component of commercial glucose (corn syrup) and no proportion of dextrose and water can be found whose freezing point is below -5°C (23°F). Solutions containing glucose behave like those containing honey in that they freeze slowly, first to slush and finally solid.

Solutions of Alcohols (including Glycerine and Glycol)

Under this heading will be considered solutions of (1) denatured alcohol, (2) wood alcohol, (3) glycerine, and (4) glycol; all of which the chemist regards as alcohols. This group includes the most satisfactory solutions for automobile radiator use which the Bureau has yet tested.

The table of freezing points on the next page was obtained from actual measurements made at the Bureau of Standards, on solutions of the following commercial materials; 180° proof denatured alcohol (90% by volume), wood alcohol (97% by volume), distilled glycerine (95% by weight), ethylene glycol (95% by weight). All the results are believed to be correct within 1°C, which is sufficiently accurate in view of the large factor of safety explained below.

The freezing point is taken to be that temperature in the cooling process at which crystals begin to form. The temperature at which the entire mass becomes solid may be several degrees lower than the freezing point of dilute solutions, and ten to fifteen degrees lower for the more concentrated solutions. For example a 30% solution of denatured alcohol begins to freeze, that is, small crystals of ice form, at +10°F but the solution does not freeze solid until a temperature of -5°F or lower is reached. Hence a temperature considerably lower than that given in the table for any given percentage of alcohol would not injure the engine or radiator. However, it seems desirable to keep the solution at such a concentration that ice crystals will not form at the lowest temperature to be encountered, since such crystals may interfere with circulation.

Table giving the freezing points and specific gravities of certain anti-freezing solutions

Percentage (by volume) in water and freezing points

Solution	10% °C	10% °F	20% °C	20% °F	30% °C	30% °F	40% °C	40% °F	50% °C	50% °F
Denatured alcohol (90% by vol.)	-3	+27	-7	+19	-12	+10	-10	-2	-28	-18
	(0.988)		(0.973)		(0.938)		(0.957)		(0.943)	
Wood alcohol (97% by vol.)	-5	+23	-12	+10	-19	-2	-29	-20	-40	-40
	(0.987)		(0.975)		(0.933)		(0.952)		(0.937)	
Distilled glycerine (95% by wt.)	-2	+29	-6	+21	-11	+12	-18	0	-26	-15
	(1.029)		(1.057)		(1.085)		(1.112)		(1.140)	
Ethylene glycol (95% by wt.)	-3	+26	-9	+16	-16	+3	-24	-11	-35	-31
	(1.016)		(1.031)		(1.045)		(1.053)		(1.070)	

Example illustrating use of table

In order to illustrate how a non-freezing solution is prepared, assume that the lowest temperature anticipated is 19 degrees above zero Fahrenheit and that denatured alcohol is to be used.

By reference to the table in the line marked "Denatured Alcohol", +19°F is found in the 20% column. If the radiator holds 3.5 gallons, 20% of this must be alcohol and the remaining 80% water; 20% of 3.5 gallons is 0.7 gallon or a little more than 5.5 pints. This amount of denatured alcohol should be added to 2.8 gallons or a little more than 11 quarts of water. A solution thus prepared should have a specific gravity of 0.978 at 60°F and will not begin to freeze until its temperature is approximately +19°F.

If the denatured alcohol to be used is 188° proof instead of 180° proof (that is, contains only 6% of water instead of 10%) the amount required will be approximately 4% less or 5.3 pints.

Denatured Alcohol

Denatured alcohol solutions are at present the most generally used radiator solutions. It is possible to get adequate protection against freezing with denatured alcohol, its solutions are not appreciably more corrosive than water, and their viscosities are comparatively low.

The chief objection to this alcohol, however, is that it continually boils out of the solution and must be replaced frequently in order to maintain adequate protection against freezing. The most practical way of determining how much protection an alcohol solution of unknown strength will give is to measure its specific gravity with a hydrometer and refer to the above table. If more protection is required, alcohol can be added until the corresponding gravity is reached. Care should be taken to have the solution thoroughly mixed and, as the specific gravities given in the table are obtained at 60°F, the specific gravity should be measured when the temperature of the solution is between 55°F and 65°F.

A convenient method of assuring fairly uniform protection over considerable periods and one which does not involve frequent specific gravity determinations is based on the following considerations: Take a 20% alcohol solution, whose freezing point is +18°F. Both alcohol and water are lost from the solution but the bulk of the loss is alcohol. The relative rate at which alcohol and water evaporate from such a solution can be determined in the laboratory. Experiment shows that this particular solution loses alcohol about three times as fast as it loses water, until its volume has decreased 10% or more. Hence the motorist using a 20% alcohol solution in his radiator can prepare a replacement solution by mixing a quart of water with three quarts of denatured alcohol and restore his radiator solution to its original strength by adding a little of this replacement solution whenever the liquid level appears low. Replacement solutions for various strengths of radiator solution are given below. The figures are percentages by volume and the alcohol used is 180° proof denatured alcohol (90% by volume).

Radiator Solution Denat. Alcohol	Radiator Solution Water	Replacement Solution Denat. Alcohol	Replacement Solution Water
10	90	60	40
20	80	75	25
30	70	82	18
40	60	87	13
50	50	90	10

Another disadvantage in the use of denatured alcohol solutions is the fact that their boiling points are appreciably lower (30°F for a 50% solution) than the boiling point of water so that average cylinder temperatures tend to be lower in winter than in summer.

Further criticisms of denatured alcohol solutions are based on the unpleasant odor of certain denaturants and the fact that nitrocellulose finishes are particularly likely to become spotted in case alcohol is splashed or spilled on them.

Wood Alcohol

Wood alcohol solutions are more volatile and have lower boiling points than the corresponding denatured alcohol solutions so most of the objections to the use of the latter apply with even more force to the use of wood alcohol. On the other hand, about 10% less wood alcohol than denatured alcohol is required for protection against freezing at any given temperature. Wood alcohol, however, sometimes contains free acid which is objectionable and for this reason should not be used unless it is known to be free from acids. In addition to being unpleasant the fumes from wood alcohol may be harmful.

Distilled Glycerine

Equal concentrations of denatured alcohol and of glycerine in water give about the same protection against freezing. The Bureau's tests, as well as more extended investigations in private laboratories, indicate that distilled glycerine solutions are no more corrosive than denatured alcohol solutions. The colorless c.p. glycerine and commercial grades of yellow distilled glycerine are equally satisfactory for radiator use. Crude glycerine, on the contrary is undesirable as it usually contains salts which promote corrosion.

Glycerine has a high boiling point and is practically non-volatile up to the boiling point of its 50% aqueous solution (225°F). Hence a glycerine solution will last for an entire season without further addition of glycerine (provided the cooling system is free from leaks.) The volume of the solution when cold should be slightly less than the full radiator capacity, otherwise the expansion of the liquid when heated will cause it to overflow with consequent waste. For the same reason, in replacing the water lost by evaporation, the radiator should be filled to a definite level at least 2 inches below the overflow pipe. If desired, the glycerine solution can be drawn off at the end of the season and saved for use a second season.

The quantity of glycerine required to give protection against freezing at various temperatures can be determined from the table on page 5, as illustrated in the case of denatured alcohol. Glycerine is miscible with water in all proportions but on account of the high specific gravity of the 95% glycerine (1.25) it is well to mix it with the water before putting it in the radiator. Some of the soap makers are selling a more dilute grade of distilled glycerine for radiator use. Proportionately more of this is required but it mixes somewhat more readily with the water.

The more concentrated glycerine solutions are distinctly more viscous than the corresponding solutions of denatured alcohol at low temperatures. This may be a disadvantage with certain types of cooling systems in very severe climates but, under average conditions, distilled glycerine appears to be superior to denatured alcohol for radiator use.

Glycerine and Alcohol

The addition of say half a gallon of glycerine and half a gallon of denatured alcohol to water makes a solution which gives slightly more protection against freezing than would be obtained by adding a gallon of glycerine or a gallon of alcohol alone. The customary use of a glycerine-alcohol-water solution has the disadvantage that both alcohol and water will evaporate from such a solution at different rates and it becomes a difficult matter to determine how much of each should be added to replace the evaporation loss.

On the other hand, where the winter temperature seldom goes below 0°F a 35 or 40 percent glycerine-water solution will ordinarily give adequate protection. Then, in case an exceptional cold wave comes and the temperature drops to -10°F it might be economy to add some alcohol for temporary additional protection rather than to add more glycerine.

Ethylene Glycol

Ethylene glycol solutions give more protection against freezing than either glycerine or denatured alcohol solutions of the same strength (see table on page 5). Like glycerine, ethylene glycol is practically non-volatile at operating temperatures and its solutions are non-corrosive. Unlike glycerine, ethylene glycol solutions are only slightly more viscous at low temperatures than denatured alcohol solutions of equal concentrations. Hence solutions of ethylene glycol appear to be superior to denatured alcohol solutions under all circumstances and, at least for very severe climates, to offer some advantages over distilled glycerine solutions.

Ethylene glycol solutions can be used for an entire season without further addition of glycol and also may be drawn off at the end of the season and saved for use again. The same precautions mentioned in the case of glycerine should be taken in filling the radiator, otherwise the expansion of the liquid when heated will cause it to overflow. The specific gravity of ethylene glycol is not high enough to necessitate mixing the glycol with water before it is put into the radiator.

Trimethylene Glycol

The only other glycol which the Bureau of Standards has tested is trimethylene glycol. The commercial material available for radiator use is a liquid containing about 85% trimethylene glycol, 12% glycerine and 3% water. Its solutions are non-corrosive and their freezing points are practically identical with those of equivalent glycerine solutions. Its solutions are intermediate in viscosity between those of glycerine and those of ethylene glycol. Its slightly lower viscosity appears to constitute its chief advantage over distilled glycerine.